Highlights from Recent Literature

1 ANALYTICAL

1.1 *Anion Exchange of Gold Chloro Complexes on Carbon Paste Electrode for Determination of Gold in Pharmaceuticals*

Anion exchange of tetrachloroaurates on a carbon paste electrode modified with montmorillonite was studied by P. Kula and Z. Navratilova of the Institute of Geonics, Academy of Sciences of Czech Republic, Ostrava, *Electroanalysis*, 2001, **13**(8-9), 795-798, regarding dependence on pH and concentration of chlorides in a sorption medium. Anion sorption of $[AuCl_4]^-$ was used as a preconcentration step to the determination of gold in a pharmaceutical preparation. The first investigation was to use this method to determine gold in blood serum. A limit of detection of 8.12×10^{-7} mol/L gold was achieved in a sample simulating an inorganic part of the serum.

1.2 *Simultaneous Determination of Gold and Palladium*

An H-point standard addition method (HPSAM), based on spectrophotometric measurement, for simultaneous determination of Au(III) and Pd(II) has been described by N. Pourreza and S. Rastegarzadeh, College of Science, Department of Chemistry, Shahid Chamran University, Ahvaz, Iran, *Anal. Chim. Acta.* 2001, **437**(2), 273-280. This method is based on the different rate of complex formation of Au(III) and Pd(II) with 5(p-dimethylaminobenzylidene)rhodanine (PDR) in the presence of formate buffer and Brij-35. A study of the rate of complex formation in various buffers was carried out and the HPSAM performed well in a formate buffer. The results showed that simultaneous determination of Pd and Au could be performed at 0.17-1.8 and 1-3 µg/mL, respectively. Selectivity was studied and the main interferences were eliminated.

This method was successfully used for the determination of the analytes in jewellery and synthetic samples.

2 CATALYSIS

2.1 *Supported Gold Catalysts for CO Oxidation: Effect of Calcination on Structure, Adsorption and Catalytic Behaviour*

M. Maciejewski, P. Fabrizioli, J.-D. Grunwaldt, O. Sven Becker and A. Baiker of the Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, Switzerland, *Phys. Chem. Chem. Phys.*, 2001, **3**(17), 3846-3855, have studied the adsorption behaviour and CO oxidation activity of TiO_2- and ZrO_2- supported gold catalysts, prepared by adsorption of gold colloids on the supports, using pulse thermal analysis and diffuse reflectance FTIR spectroscopy. Structural investigations using transmission electron microscopy, X-ray diffraction and XPS showed that gold particles, mainly in the metallic state and with similar particle size distribution (2.0-3.0 nm), could be prepared on both supports, but the as-prepared samples contained carbonaceous impurities from the preparation procedure. During calcination in 20 vol% oxygen/He only slight sintering occurred up to 600°C. Above 600°C, the gold particles sintered on both supports. CO oxidation activity, studied by injection of CO pulses into an oxygen stream in the thermoanalyser, depended strongly on the calcination temperature of the catalysts.

Maximum activity was obtained for the catalysts calcined at 500°C (Au/TiO_2) and 560°C (Au/ZrO_2), respectively. Catalysts calcined at higher temperatures exhibited lower activity due to sintering of the gold particles. CO adsorption was found to be weak on both catalyst systems. No significant adsorption of O_2 and CO_2 could be detected by pulse thermal analysis. CO adsorption increased for catalysts calcined up to 200-400°C. Calcination temperatures leading to maximum CO adsorption did not coincide with calcination temperatures affording maximum CO oxidation activity. Moreover, the removal of carbonaceous residues during calcination was found to be correlated with the activity. The results of the adsorption studies do not support a Mars-van Krevelen mechanism, where lattice oxygen would be involved. CO oxidation by the reaction of adsorbed CO with molecularly adsorbed oxygen seems more likely.

2.2 *Catalytic Activity of $Rh_2Cl_2(CO)_4$ Adsorbed and Tethered on Gold Powder. IR Spectroscopic Characterization and Olefin Hydrogenation Activity*

H. Gao and R.J. Angelici, Ames Laboratory and Department of Chemistry, Iowa State University, USA, *Can. J. Chem.*, 2001, **79**(5/6), 578-586, have prepared catalysts by adsorbing $Rh_2Cl_2(CO)_4$ directly on gold powder or on gold that contained the tethered ligands 2-(diphenylphosphino)ethane-1-thiol (DPET) or methyl 2-mercaptonicotinate (MMNT). IR studies (diffuse reflectance IR Fourier transform (DRIFT)) of the catalyst Rh-Au prepared by adsorbing $Rh_2Cl_2(CO)_4$ directly onto gold indicate that an $Rh(CO)_2$ species is present. IR studies of Rh-DPET-Au suggest that tethered cis-$Rh(DPET)(CO)_2Cl$ is the major species at relatively high $Rh_2Cl_2(CO)_4$ loadings, but trans-$Rh(DPET)_2(CO)Cl$ is observable at low $Rh_2Cl_2(CO)_4$ loadings. Spectral investigations of the catalyst Rh-MMNT-Au prepared by adsorbing

$Rh_2Cl_2(CO)_4$ on MMNT-Au suggest that tethered [cis-$Rh(MMNT)_2(CO)_2]^+Cl^-$ and (or) $Rh(MMNT)(CO)_2Cl$ are the major species at low $Rh_2Cl_2(CO)_4$ loadings, while a new unidentified species predominates at high $Rh_2Cl_2(CO)_4$ loadings.

All three catalysts are active for 1-hexene hydrogenation under the mild conditions 40°C and 1 atm of H_2; they are much more active than Au powder or $Rh_2Cl_2(CO)_4$ in solution. Of the three catalysts, Rh-Au is the most active with a maximum turnover frequency (TOF) of 800 mol H_2 per mol Rh per min while its turnover (TO) is 29 600 mol H_2 per mol Rh during a 2-h run. Under the conditions of 1-hexene hydrogenation, the catalysts lose their CO ligands. Thus, it appears that a form of Rh metal on Au is the catalytically active species.

2.3 Carbon Monoxide Oxidation on Gold Surfaces Studied on the Atomic Scale

The interaction of small gold crystal tips with oxygen gas and CO/O_2 gas mixtures has been studied by T. Bar, T.V. De Bocarme, B.E. Nieuwenhuys and N. Kruse, Chemical Physics of Materials, Université Libre de Bruxelles, Belgium, *Catal. Lett.*, 2001, **74**(3-4), 127-131, using field ion microscopy (FIM). High-resolution FIM-images of clean tips were obtained with hydrogen and neon as imaging gas. Between 300 and 450 K the exposure of a clean gold sample to O_2 gas at 100-1000 mbar, in the absence of an electric field, led to oxygen chemisorption and formation of a 'surface oxide'. The presence of an electric field of 12-15 V/nm was found to enhance the oxidation process. Exposure to CO gas at 300 K led to the removal of the surface oxide. This was associated with the occurrence of a wave front which started in the apex centre and extended to the outskirts of the tip sample. The build-up of the surface oxide and its titration by carbon monoxide was completely reversible. Our results strongly suggest that pure gold crystals are active catalysts for CO oxidation at 300 K.

2.4 Epoxidation of Propylene over Gold Catalysts Supported on Non-Porous Silica

Non-porous silica has been used as a carrier of Au/Ti-SiO_2 catalysts for the direct vapour-phase epoxidation of propylene in the presence of both hydrogen and oxygen (C. Qi, T. Akita, M. Okumura and M. Haruta, Interdisciplinary Basic Research Section, AIST, Osaka National Research Institute, Ikeda, Japan, *Appl. Catal., A*, 2001, **218**(1-2), 81-89). The smooth surfaces were expected to facilitate the desorption of propylene oxide (PO). Their catalytic performances were, however, inferior to those of Au/TS-1 and Au/Ti-MCM catalysts, but an interesting feature was that propylene epoxidation over Au/Ti-SiO_2 depends on the calcination temperature of the Ti-SiO_2 support. Higher calcination temperature benefits PO production at reaction temperatures above 100°C. IR and HRTEM analyses showed that the interaction between titanium oxides and silica was intensified to form more isolated TiO_4 units with tetrahedral coordination on the surfaces of Ti-SiO_2 supports with an increase in heat treatment temperature. These isolated TiO_4 sites incorporated in silica surface layers are assumed to be an important structural factor for the selective deposition of gold particles and selective PO formation.

2.5 Au/TiO_2 Nanostructured Catalyst: Effects of Gold Particle Sizes on CO oxidation at 90 K

An FTIR study of CO adsorption and oxidation at 90 K on gold-titania catalysts has been reported by F. Boccuzzi, A. Chiorino and M. Manzoli, Universita di Torino, Dipartimento di Chimica I.F.M., Italy, *Mater. Sci. Eng., C*, 2001, **C15**(1-2), 215-217. Three nanostructured Au/TiO_2 catalysts were used, with the same gold loading, calcined at three different temperatures. and with different gold particle mean sizes of 2.4, 2.5 and 10.6 nm. On all the samples, the CO adsorption and different CO-$^{18}O_2$ interactions were examined. From the experimental results, it can be deduced that: (i) at 90 K, carbon monoxide and oxygen are molecularly and competitively adsorbed on gold step sites; (ii) $C^{16}O^{18}O$ formation occurs if carbon monoxide is pre-adsorbed on the calcined small particles, while it is almost completely inhibited if oxygen is pre-adsorbed; and (iii) on the sample with 10.6 nm particles, the reaction does not occur at all at 90 K. The role of the concentration of step sites on the mechanism of the reaction is discussed.

2.6 Enhanced Photocatalytic Activity of Gold Ion and Gold Modified Titania

F.-B. Li, G.-B. Gu, G.-F. Huang, X.-J. Li and H.F. Wan, Guangdong Institute of Eco-Environment and Soil Science, Canton, P.R. China, *J. Environ. Sci. (China)*, 2001, **13**(2), 201-204, prepared Au ion modified TiO_2 using a sol-gel technique and Au deposited on TiO_2 by photo-reduction. The physical properties were influenced significantly by the presence of Au ion or Au. The enhanced photo-activity of Au modified TiO_2 was quantified in terms of methylene blue degradation. The presence of Au ion in TiO_2 lattices or Au on a TiO_2 surface enhanced their photo-activity. The optimum molar content of Au ion doping and Au deposition was 0.5%. The 1st-order rate constants for Au modified TiO_2 was more than that of pure TiO_2, and decreased by increasing the content of Au ion and Au when their contents were >0.5%. Gold ion doped in TiO_2 lattices was more effective to enhancing the photo-activity than Au on the TiO_2 surface. The relationship between physical properties, chemical properties and photo-activity was discussed (see also F.-B. Li, X.-Z. Li, X.-J. Li and H.-F. Wan, *Huaxue Xuebao*, 2001, **59**(7), 1072-1077).

2.7 Deposition of Gold Nanoparticles Using an Organogold Complex

In order to develop a new preparation method with a wide application to a wide variety of supports, a gas phase grafting

method was examined using an organo-gold complex. M. Okumura, S. Tsubota and M. Haruta, of the Osaka National Research Institute, AIST, Ikeda, Japan, Phys. Chem. Clusters, Proc. Nobel Symp., 117th (2001), Meeting Date 2000, 307-308, ed. E.E.B. Campbell and M. Larsson, World Scientific Publishing Co. Pte. Ltd., Singapore, have shown that using this method, gold nanoparticles can be deposited on a wide variety of metal oxide and other supports such as active carbon.

2.8 Scanning Tunneling Microscopy of Gold Clusters on TiO_2(110). CO Oxidation at Elevated Pressures

A. Kolmakov and D.W. Goodman, Department of Chemistry, Texas A&M University, College Station, TX, USA, *Surf. Sci.*, 2001, **490**(1-2), L597-L601, have studied the *in-situ* imaging of individual supported gold nanoparticles with scanning tunneling microscopy at elevated temperatures while changing the ambient pressure of the reactants over *ca* 10 orders of magnitude. The morphological changes of the Au-TiO_2 interface were studied under CO oxidation reaction conditions. The changes in metal cluster size and TiO_2 surface re-growth were observed during pressure excursions of the CO and O_2 reactants from 1 x 10^{-8} - 665 Pa (see also A. Kolmakov and D.W. Goodman, *Catal. Lett.*, 2000, **70**(3,4), 93-97).

2.9 Novel Preparation Method and Characterization of Au-Fe/HY Zeolite Containing Highly Stable Gold Nanoparticles inside Zeolite Supercages

A sample of 1%Au-0.5%Fe/HY has been prepared by D. Horvath, M. Polisset-Thfoin, J. Fraissard and L. Guczi of the Institute of Isotope and Surface Chemistry, Department of Surface Chemistry and Catalysis, HAS, Chemical Research Centre, Budapest, Hungary, *Solid State Ionics*, 2001, **141-142**, 153-156, by coexchange in HY zeolite using Fe(II)ethylenediammonium and Au(III)ethylenediamine complex-ions. Highly stable gold nanoparticles inside zeolite supercages were formed by autoreduction. Monometallic Au and Fe samples were also prepared by ion exchange. ^{129}Xe NMR and TEM studies revealed metallic gold nanoparticles along with Fe cations inside the zeolite supercages. Neither the presence of metallic Au nor Fe can be detected by XPS, which is indicative of the presence of both metals being inside the zeolite cavities. In the CO oxidation reaction, the Au-Fe/HY sample possessed the highest activity.

2.10 A Nanoscale Model Catalyst Preparation: Solution Deposition of Phosphine-Stabilized Gold Clusters onto a Planar TiO_2(110) Support

Agglomeration of noble metal particles has been a long-standing obstacle in the preparation of planar, finely dispersed, metal cluster-oxide support model catalyst systems. A solution deposition method has therefore been devised by C.C. Chusuei, X. Lai, K.A. Davis, E.K. Bowers, J.P. Fackler and D.W. Goodman, Department of Chemistry, Texas A&M University, College Station, USA, *Langmuir*, 2001, **17**(13), 4113-4117. Six-atom gold clusters, in the form of $[Au_6(PPh_3)_6][BF_4]_2$ (Au_6L_6), were deposited onto a TiO_2(110) single crystal after an acetone pretreatment of the substrate and examined with scanning tunneling microscopy (STM), high-resolution electron energy loss spectroscopy (HREELS), and XPS (XPS). STM revealed single-unit entities of clusters *ca* 1 nm in height, corresponding to the six-atom Au centre with the triphenylphosphine ligands attached.

As a check on the success of the homogeneous dispersion, electron-stimulated desorption (ESD) was performed, irradiating the TiO_2(110) surface with a 0.12 C cm^{-2} electron beam flux followed by STM, HREELS, and XPS. Evidence for ligand removal was shown by a pronounced reduction in height in the STM, a disappearance of the aromatic $\nu_{C\text{-}H}$ intensity at *ca* 3000 cm^{-1} in the HREEL spectra, and a +0.4 eV shift in the XPS Au $4f_{7/2}$ core level.

3 CHEMISTRY

3.1 Ternary Rare Earth Gold Compounds

R. Mishra, R. Pottgen, R.-D. Hoffmann, D. Kaczorowski, H. Piotrowski, P. Mayer, C. Rosenhahn and B.D. Mosel, Department Chemie, Universität Munchen, Germany, *Z. Anorg. Allg. Chem.*, 2001, **627**(6), 1283-1291, have prepared new intermetallic rare earth compounds, REAuCd (RE = Y, La-Nd, Sm-Yb) and RE_2Au_2Cd (RE = La, Pr, Nd, Sm) by reaction of the elements in sealed Ta tubes in a high-frequency furnace. The compounds were studied by x-ray diffraction both as powders and single crystals. Susceptibility measurements show Pauli paramagnetism for YbAuCd and Curie-Weiss behaviour >100 K for EuAuCd with an experimental magnetic moment of 7.86(6) μB/Eu.

Ferromagnetic ordering is detected at 28 K. The saturation magnetic moment is 7.1(1) μB/Eu at 1.9 K. ^{151}Eu Mössbauer spectra show an isomer shift of -9.2(2) mm/s and full magnetic hyperfine field splitting at 4.2 K with an internal hyperfine field of 19.5(4) T at the Eu nuclei. The RE_2Au_2Cd compounds crystallize with the Mo_2FeB_2 structure, the ternary ordered version of the U_3Si_2 type. These structures may be considered as an intergrowth of distorted CsCl and AlB_2 related slabs RECd and $REAu_2$. Chemical bonding in REAuCd and RE_2Au_2Cd is briefly discussed (see also Y. Ning, *Gold Bull.*, 2001, **34**, 77 - 88).

3.2 Synthesis of Luminescent Trinuclear Gold(I) Derivatives with a Triphosphine and S-Donor Ligands

Trinuclear Au(I) complexes have been prepared by M. Bardaji and A. Laguna, Instituto de Ciencia de Materiales de Aragon, Departamento de Quimica Inorganica, Universidad de Zaragoza-CSIC, Spain, *Inorg. Chim. Acta*, 2001, **318**(1,2), 38-44 containing bis(diphenylphosphinomethyl)phenylphosphine

(dpmp) and several anionic S-donor ligands. For example, the reaction of $[(AuCl)_3(\mu\text{-dpmp})]$ with K Et xanthate afforded the trinuclear Au(I) complexes $[Au_3Cl_{3-x}(S_2COEt)_x(\mu\text{-dpmp})]$ (x = 1, 2, 3). These complexes were readily transformed by reaction with silver triflate into $[Au_3Cl_{2-x}(S_2COEt)_x(\mu\text{-dpmp})](CF_3SO_3)$ (x = 1, 2). Studies of the optical properties of these derivatives indicate that most of them luminesce in the solid state at room temperature with emission maxima in the range 510-545, while at low temperature all are luminescent with emission maxima ranging from 480 to 545 (see also E.J. Fernández, A. Laguna and J.M. López-de-Luzuriaga, *Gold Bull.*, 2001, **34**, 14 - 19).

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 Use of Gold Nanospheres to Study Defect Evolution in Thin Films

A technique has been described by P.B. Mirkarimi, S.L. Baker and D.G. Stearns of the Lawrence Livermore National Laboratory, CA, USA, *J. Vac. Sci. Technol., B*, 2001, **19**(3), 628-633, in which commercially available colloidal gold solution is used to deposit monodisperse gold nanospheres with diameters ranging from 20 to 60 nm directly onto Si wafers. The technique for depositing the gold nanospheres is straightforward and requires little in terms of infrastructure or resources. The wafers containing the gold nanospheres were first characterized by techniques such as atomic force microscopy and TEM, after which they are coated with a thin film and re-characterized. This enables a quantitative study of the evolution of thin-film defects nucleated by small substrate particles. An example is provided where the technique is used to study the evolution of defects in Mo/Si multilayer films, and this is of significant importance in the development of reticles for extreme UV lithography.

4.2 Quantitative Characterization of Obliquely-Deposited Substrates of Gold by Atomic Force Microscopy

N.L. Abbott and J.J. Skaife and The Regents of the University of California, USA, have patented (US Patent 6288392 B1, 11 September, 2001) a method involving use of scanning probe microscopy to quantitatively characterize structural anisotropy within obliquely deposited metal films. Whereas visual inspection of AFM images (real space or reciprocal space) reveals no obvious structural anisotropy within these gold films, by quantitative analysis of the AFM profiles, subtle structural anisotropy is observed. The quantitative characterization provides a method for the estimation of the influence of anisotropy on the orientations of supported mesogenic layers.

5 COLLOIDS AND NANOTECHNOLOGY

5.1 Properties and Characterization of Gold Nanowires

Gold nanowires a few atomic diameters wide were observed by ultra-high vacuum transmission electron microscopy, and their conductance measured simultaneously using a scanning tunnelling microscope built into the electron microscope (K. Takayanagi, Y. Kondo and H. Ohnishi, Graduate School of Interdisciplinary Science and Technology, Tokyo Institute of Technology, Yokohama, Japan, *JSAP Int.*, 2001, **3**, 3-8). A strand of gold atoms suspended between electrodes was observed to have a conductance of 2e2/h (=12.9 $k\omega^{-1}$), where e is the electron charge and h is Planck's constant. This conductance quantization results from ballistic transport of electrons through a conduction channel of the strand.

5.2 Mechanical Properties of a Gold Wire of Single Gold Atoms

G. Rubio-Bollinger, S.R. Bahn, N. Agrait, K.W. Jacobsen and S. Vieira of the Instituto Universitario de Ciencia de Materiales "Nicolas Cabrera", Departamento Fisica de la Materia Condensada C-III, Laboratorio de Bajas Temperaturas, Universidad Autonoma de Madrid, Spain, *Phys. Rev. Lett.*, 2001, **87**(2), 026101/1-026101/4, have used a scanning tunnelling microscope supplemented with a force sensor to study the mechanical properties of a metal nanostructure consisting of a freely suspended chain of single gold atoms. The bond strength of the nanowire is about twice that of a bulk metallic bond. *Ab initio* calculations of the force at chain fracture were performed and compared quantitatively with experimental measurements. The mechanical failure and nanoelastic processes observed involved during atom wire fabrication were investigated using molecular dynamics simulations. The total effective stiffness of the nanostructure is strongly affected by the detailed local atomic arrangement at the chain bases.

5.3 Self-Organization of Large Gold Nanoparticle Arrays

Conditions have been described that enable large (16-170 nm) gold particles to self-organize at an air-water interface into monoparticulate films which can be subsequently transferred onto substrates as 2D hexagonal close-packed arrays. The surfactant chosen by B. Kim, S.L. Tripp and A. Wei, Department of Chemistry, Purdue University, West Lafayette, IN, USA, *J. Am. Chem. Soc.*, 2001, **123**(32), 7955-7956, was resorcinarene tetrathiol which is ideal for promoting the formation of the arrays with periodicities >170 nm. The self-assembly of large gold particles was achieved with structural precision and has excellent potential for the fabrication of nanostructured films with tunable optical and optoelectronic

properties. The large gold nanoparticle arrays are especially promising as substrates for surface-enhanced Raman scattering (SERS).

5.4 Magnetic Circular Dichroism Spectra for Colloidal Gold Nanoparticles in Xerogels at 5.5 K

Colloidal gold nanoparticles (*ca* 25 nm) and $Au_9(PPh_3)_8^{3+}$ complex ions (<2 nm) were separately encapsulated in optically transparent xerogels. M.A. Zaitoun, W.R. Mason and C.T. Lin of the Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, USA, *J. Phys. Chem. B*, 2001, **105**(29), 6780-6784, have shown that the high quality xerogel is isotropic with no material strain or birefringence that would interfere with the Magnetic Circular Dichroism (MCD) measurements. The MCD and absorption spectra for the surface plasmon band at 523 nm for *ca* 25 nm gold nanoparticles and for the $Au_9(PPh_3)_8^{3+}$ cluster complex ion in the spectral region of 600-400 nm were examined at 5.5-295 K.

5.5 Size-Dependent Solubility of Thiol-Derivatized Gold Nanoparticles in Supercritical Ethane

N.Z. Clarke, C. Waters, K.A. Johnson, J. Satherley and D.J. Schiffrin of the Department of Chemistry, University of Liverpool, UK, *Langmuir,* 2001, **17**(20), 6048-6050, have shown that alkane thiol-capped gold nanoparticles can be dissolved in supercritical ethane. The solubility was found to be dependent on the core diameter thus allowing separation by size. Nanoparticles with a core diameter less than 1.7 nm were soluble in the supercritical fluid.

5.6 Thermal Maps of Gold Micro-Stripes Obtained Using Scanning Force Microscopy

Two ways of measuring current maps on gold micro-stripes on a nanometric scale have been demonstrated by P.J. de Pablo, J. Colchero, J. Gomez-Herrero, P.A. Serena and A.M. Baro, Laboratorio de Nuevas Microscopias, Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Spain, *Nanotechnology*, 2001, **12**(2), 113-117. In the first one, an alternating current is applied to the stripe and the thermal expansion of the tip-sample system is registered by the cantilever. In the second, maps of adhesion of the surface are acquired simultaneously with the topography. The adhesion force map varies with the temperature because it depends mainly on the water meniscus between tip and sample, and the size of the meniscus depends on the temperature.

5.7 Preparation of Gold Nanoparticles from a Polyelectrolyte Complex Solution of Terthiophene Amphiphiles

J.H. Youk, J. Locklin, C. Xia, M.K. Park and R. Advincula, Department of Chemistry, University of Alabama at Birmingham, USA, *Langmuir*, 2001, **17**(15), 4681-4683, have reported the preparation of gold nanoparticles in aqueous solutions using a polyelectrolyte that possesses pendant reducing groups. A polyelectrolyte complex (PEC) with water soluble terthiophene derivatives was used for the reduction of $HAuCl_4$ to gold nanoparticles.

6 ELECTROCHEMISTRY

6.1 Auto-Inhibition of Hydrogen Gas Evolution on Gold in Aqueous Acid Solution

Dramatic changes in the redox behaviour of gold/aqueous solution interfaces have been observed by following either cathodic or thermal electrode pretreatment (L.D. Burke, A.P. O'Mullane, V.E. Lodge and M.B. Mooney, Chemistry Department, National University of Ireland, Cork, *J. Solid State Electrochem.*, 2001, **5**(5), 319-327). Further work on the cathodic pretreatment of gold in acid solution revealed that as the activity of the gold surface was increased, its performance as a substrate for hydrogen gas evolution under constant potential conditions deteriorated. The change in activity of the gold atoms at the interface, which was attributed to a hydrogen embrittlement process (its occurrence was subsequently checked by surface microscopy), was confirmed, as in earlier work, by the appearance of a substantial anodic peak at *ca* 0.5 V (RHE) in a post-activation positive sweep. Changes in the catalytic activity of a metal surface reflect the fact that the structure, or topographical, thermodynamic activity and electronic properties of a surface, are dependent not only on pretreatment but also, in the case of the hydrogen evolution reaction, vary with time during the course of the reaction. As will be reported shortly, similar (and often more dramatic) time-dependent behaviour was observed for hydrogen gas evolution on other metal electrodes.

6.2 The Effect of Severe Thermal Pretreatment on the Redox Behaviour of Gold in Aqueous Acid Solution

L.D. Burke, L.M. Hurley, V.E. Lodge and M.B. Mooney of the Chemistry Department, National University of Ireland, Cork, *J. Solid State Electrochem.*, 2001, **5**(4), 250-260, have shown that severe thermal pretreatment of gold wire electrodes in an inert gas atmosphere resulted in the appearance of dramatic premonolayer oxidation responses, which in some instances commenced at 0.25 V (RHE), for the resulting active gold electrodes in aqueous acid media. Similar behaviour was reported earlier for platinum and gold activated by cathodic pretreatment in acid solution; these active noble metal surfaces are evidently more susceptible to oxidation than bulk copper. Such behaviour was attributed to the effect of surface disorder; many of the metal atoms at the interface are assumed to be in a very active, metastable state possessing quite low lattice stabilization energy. Premonolayer oxidation responses are again correlated with electrocatalytic behaviour and the existence of

unusual chemisorption behaviour for molecules reacting at highly active states of metals is outlined (see also L.D. Burke and P.F. Nugent, *Gold Bull.*, 1997, **30**, 43 - 53; 1998, **31**, 39 - 50).

6.3 Effect of $Au(CN)^{2-}$ on the Anodic Oxidation of Gold in Phosphate Electrolytes

The effect of $Au(CN)^{2-}$ anions on the anodic oxidation of gold has been studied by K. Juodkazis, J. Juodkazyte and T. Juodiene of the Laboratory of Precious Metals Electrochemistry, Institute of Chemistry, Vilnius, Lithuania, *Chemija*, 2000, **11**(4), 180-185, in 0.5M H_3PO_4 + KOH solutions. This process is considerably inhibited in the E region from *ca* 0.7 V to *ca* 1.2 V in slightly acid and neutral solutions containing $Au(CN)^{2-}$. The inhibition begins at E values prior to the onset of gold anodic oxidation. In the solutions containing $Au(CN)^{2-}$, insoluble Au(III) cyanide can be formed as a result of AuCN oxidation on the gold electrode surface. This Au(III) cyanide passivates the gold electrode and inhibits the process of anodic oxidation. In alkaline solution the presence of $Au(CN)^{2-}$ does not hinder the $Au(OH)_3$ surface layer formation significantly, since in this case Au(III) cyanide is unstable on the gold electrode surface.

7 ELECTRONICS

7.1 Ceramic Circuit Boards with Gold Wire-Bonding of Semiconductor Devices to Thick Conductor Films

A patent by K. Miyashita, M. Asano, K. Nakatsuru, Kunihito and H. Matsumoto, Hitachi Ltd., Japan, Hitachi Car Engineering K. K., Japanese Patent 2001244378 A2, 9 September 2001, covers circuit wiring, a conductor for gold wire-bonding, and a conductor for mounting a resistor/capacitor chip on the title ceramic substrate, provided as a Ag-Pt alloy single common thick-film which is formed by screen-printing and sintering. The Ag-Pt alloy conductor thick film provides secure gold wire-bonding adhesion without use of an gold or palladium paste.

7.2 Aggregation and Sticking Probability of Gold on Tungsten Trioxide Films

Both SEM and TEM images show that gold layers, 0.8-3.2 nm thick, deposited on WO_3 films aggregate into particles at temperatures >400°C. L.J. LeGore, R.J. Lad, J.F. Vetelino, B.G. Frederick and E.A. Kenik, Laboratory for Surface Science and Technology, University of Maine, Orono, ME, USA, *Sens. Actuators, B*, 2001, **B76**(1-3), 373-379, have shown that particle size distributions indicate that the growth mechanism is coalescence due to island mobility rather than Ostwald ripening. Both SEM and x-ray photoemission spectroscopy (XPS) analysis indicate that the amount of gold deposited on the surface is *ca* 50% of the value as determined by the quartz crystal monitor (QCM) during deposition. This difference is believed to be due to a low initial sticking probability of gold on the WO_3 surface during deposition. Finding means to create and stabilize metal particles of the optimum size remains a problem in the fields of catalysis and gas sensors.

7.3 Selective Nucleation and Area Selective OMCVD of Gold on Patterned Self-Assembled Organic Monolayers

R.A. Fischer, C. Winter, U. Weckenmann, J. Kashammer, V. Scheumann and S. Mittler, Anorganische Chemie II, Ruhr-Universität, Bochum, Germany, *Proc. - Electrochem. Soc.,* 2000, 2000-13(CVD XV), 474-488, have demonstrated the area selective organometallic CVD (OMCVD) of gold clusters and layers using trimethylphospine-methylgold Me_3PAuCH_3 as gold source onto self-assembled monolayers (SAMs) of ω-functionalized long-chain alkanethiols on gold- and silver-coated silicon and mica samples.

The dependence of surface coverage with gold nano-clusters on the reaction time is analysed by atomic force microscopy (AFM). XPS shows that nucleation and growth only occurs on thiol functionalized surfaces and not on methyl or hydroxyl functionalized SAMs. The selectivity of the growth is completely lost if gold is deposited by thermal evaporation of the pure metal as shown in direct comparison with the OMCVD method employing mixed SAMs of different surface reactivity (-SH *vs* -CH_3) that were patterned by microcontact printing.

8 MATERIALS SCIENCE

8.1 Electroless Nickel/Immersion Gold to Enhance the Reliability of the Solder Joint Strength

The interlayer between the solder and electroless Ni/Au plating and the bonding strength have been correlated by Y. Watanabe, IBIDEN Co., Ltd., Ogaki-shi, Gifu, Japan, *Hyomen Gijutsu*, 2001, **52**(5), 379-381. The bonding strength becomes smaller as the interlayer becomes thicker. The important control items in the electroless Ni/Au plating bath for obtaining stable solder bonding strength are pH, concentration, liquid circulation and vibration of the nickel bath and gold concentration and stabilizer concentration in the gold bath.

8.2 Semiconducting La_2AuP_3, the Metallic Conductor Ce_2AuP_3, and other Rare-Earth Gold Phosphides Ln_2AuP_3 with Two Closely Related Crystal Structures

M. Eschen, G. Kotzyba, B. Kunnen and W. Jeitschko, Anorg.-Chem. Inst., Westfal. Wilhelms-Univ., Munster, Germany, *Z. Anorg. Allg. Chem.*, 2001, **627**(7), 1699-1708, have synthesized the compounds Ln_2AuP_3 by reaction of the elemental components in evacuated silica tubes. Their crystal structures were determined from single-crystal diffractometer data.

La_2AuP_3 is a diamagnetic semiconductor. Pr_2AuP_3 is semiconducting with an antiferromagnetic ground state,

showing metamagnetism with a critical field of B_c = 0.5(±0.1) T. In contrast, the cerium compound is a metallic conductor, even though its cell volume indicates that the cerium atoms are essentially trivalent, as is also suggested by the ferro- or ferrimagnetic behaviour of the compound.

9 METALLURGY

9.1 Electron Confinement in Surface States on a Stepped Gold Surface Revealed by Angle-Resolved Photoemission

STM images show that vicinal Au(788) surfaces consist of a uniform array of (111)-oriented terraces of similar width (*ca* 3.8 nm) (A. Mugarza, A. Mascaraque, V. Perez-Dieste, V. Repain, S. Rousset, F.J. Garcia de Abajo and J.E. Ortega, Departamento de Fisica Aplicada I, Universidad del Pais Vasco, San Sebastian, Spain, *Phys. Rev. Lett.*, 2001, **87**(10), 107601/1-107601/4). This uniformity makes it possible to study the electronic structure of the resulting step superlattice by angle-resolved photoemission. For this terrace array the surface state appears to be broken up into 1D quantum-well levels, indicating total electron confinement within the terraces. The angular resolution allows the probability density of the terrace quantum well state to be mapped in reciprocal space, complementing nicely the wave function measured in real space by STM.

10 REFINING

10.1 Gold Process Modelling. I. Batch Modelling of the Processes of Leaching, Preg-Robbing and Adsorption onto Activated Carbon

An overall batch model has been developed by K.L. Rees and J.S.J. Van Deventer of the Department of Chemical Engineering, The University of Melbourne, Victoria, Australia, *Miner. Eng.*, 2001, **14**(7), 753-773, to describe the simultaneous processes of leaching, preg-robbing and adsorption of gold onto activated carbon. These processes were quantified for an oxide ore and three sulfide ores, which consisted of a flotation feed, and pyrite and copper concentration. The effect of the kinetics of preg-robbing on gold extraction with or without activated carbon was also closely examined for these ores.

A variable-order empirical Mintek-type model described the leaching, while the film diffusion equation with a Freundlich isotherm was used to describe both the preg-robbing at the ore surface and adsorption of aurocyanide onto activated carbon. The model developed fitted the observed experimental data well, and was used to decouple preg-robbing from leaching for the refractory ores and simulate the simultaneous leaching, adsorption and preg-robbing processes. Overall the most important factor governing the extraction of gold was the relative rates of leaching, adsorption and preg-robbing.

10.2 Laboratory Procedure to Characterize Gravity-Recoverable Gold

A test to characterize the amount of gravity-recoverable gold (GRD) in an ore has been described by A.R. Laplante, F. Woodcock and L. Huang, Department of Mining and Metallurgical Engineering, McGill University, Montreal, QC, Canada, *Trans. Soc. Min., Metall., Explor.*, 2001, Volume Date 2000, **308**, 53-59. Typical GRG results are given and possible uses discussed. The overall database, which includes 68 complete tests, is presented. The ore samples treated had an average GRG content of 63% of the total gold in the sample, with a standard deviation of 20 and a range of 3 to 97%. Both the F80 of gold and the GRG content at a grind of 100% finer than 850 µm correlate well with the overall GRG content (at 80% finer than 75 µm). The primary use of the test is to determine whether gravity recovery should be used and how. Results can also be used to predict gravity recovery, as many of the ores tested are from plants employing gravity recovery. Gravity-circuit simulation can be used to refine recovery estimates or for optimization studies.

10.3 Developments at Irgiredmet Institute in the Area of Gold Biometallurgy

Research carried out by Irgiredmet over many years in the area of gold biometallurgy have been reviewed by V.V. Lodeischikov and A.F. Panchenko, *Tsvetn. Met.(Moscow)*, 2001, (5), 20-22. The principal areas covered were: bioleaching of gold by heterotrophic bacteria and by their metabolic products, leaching with fungi, bioheterocoagulation and bioflotation of powder and colloidal gold from slime ore pulps, bioleaching of gold-containing sulfides with gold liberation by autotrophic sulfur and iron-oxidizing bacteria.